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IN SITU OBSERVATIONS OF ClO IN THE ANTARCTIC: EVIDENCE FOR CHLORINE CATALYZED DESTRUCTION OF OZONE

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Results from a series of twelve ER-2 aircraft flights into the Antarctic polar vortex are summarized. These in situ data define the spatial and temporal distribution of ClO as the aircraft flew at an altitude of ~ 18 km from Punta Arenas (54°S latitude) to the base of the Palmer Peninsula (72°S latitude), executed a rapid descent to ~ 13 km, turned north and climbed back to ~ 18 km, returning to Punta Arenas. A general pattern in the ClO distribution is reported: mixing ratios of approximately 10 ppt are found at altitude in the vicinity of 55°S increasing to 50 ppt at 60°S. In the vicinity of 65°S latitude a steep gradient in the ClO mixing ratio is observed. At a fixed potential temperature, the ClO mixing ratio through this sharp transition increases by an order of magnitude within a very few degrees of latitude, thus defining the edge of a "chemical containment vessel." From the edge of that containment vessel to the southern extension of the flights, 72°S, a dome of slowly increasing ClO best describes the distribution. Peak mixing ratios at 18

km at the southern extension of the flight track increased to 1.2 ppbv by 22 September. This corresponds to approximately 500 times the ClO mixing ratio observed at comparable altitudes at midlatitude.

At the southernmost extent of the aircraft trajectories (~ 72°S latitude) the vertical scan revealed the following gradient in ClO mixing ratio with potential temperature: 1.2 ppbv @ 450°K, 1.0 ppbv @ 440°K, 0.9 ppbv @ 430°K, 0.8 ppbv @ 420°K, 0.7 ppbv @ 410°K, 0.5 ppbv @ 400°K, 0.4 ppbv @ 390°K, 0.3 ppbv @ 380°K, 0.25 ppbv @ 370°K, 0.2 ppbv @ 360°K, 0.1 ppbv @ 350°K.

It is demonstrated using data from the first flights (17, 18 and 23 August) that in the region of high ClO, poleward of the containment vessel wall, ozone emerges from the austral polar night largely unperturbed, with little distinction between concentration observed inside (poleward) and outside (equatorward) of the chemical containment vessel wall. During the first three weeks of September, this condition alters dramatically such that by the flight of 16 September, ozone has dropped by a factor of two within the chemical containment vessel with further erosion occurring to the end of the mission on 22 September. Through the wall of the containment vessel which clearly defines the spatial transition from unperturbed ozone (and low ClO) equatorward to dramatically reduced ozone (and high ClO) poleward of the vessel wall, both ozone and ClO execute large fluctuations in mixing ratio (a factor of 2 to 3) on surfaces of constant potential temperature and in all cases these fluctuations are strongly negatively correlated.

Based upon observed concentrations of ClO as a function of latitude, altitude and time, the rate of ozone removal based on the dimerization mechanism

$$ClO + ClO \rightarrow ClOOCl$$

$$ClOOCl + h\nu \rightarrow Cl + ClOO$$

$$ClOO + M \rightarrow Cl + O_2 + M$$

$$\underline{2 \times (Cl + O_3 \rightarrow ClO + O_2)\quad}$$

$$Net: \quad 2O_3 \rightarrow 3O_2$$

is compared with the observed rate of ozone disappearance. The rate determining step is taken to be $ClO + ClO \rightarrow ClOOCl$ with a rate of

$$d[O_3]/dt = 2k^{III}[M][ClO]^2$$

A radiative transfer model is used to calculate the "waveform" of ClO as a function of solar zenith angle which is then normalized to the observed concentration of $[ClO]$ to determine

$$\Delta O_3 = 2\int k^{III}[M][ClO]^2 dt$$

for each day from early August through the end of the mission. Comparison between (1) the rate determining step in the above catalytic cycle based on observed $[ClO]$ and (2) the observed rate of ozone loss at the 450°K, 440°K, 430°K, 420°K, 410°K, 400°K, 390°K, 380°K, 370°K and 360°K potential temperature surfaces demonstrates that, within experimental uncertainty, the observed rate of ozone loss is consistent with the rate limiting step from the 450°K surface to below the 400°K surface.

We conclude the following:

1. ClO concentrations define the edge of a chemical containment vessel which mimics the position of the Antarctic polar votex.
2. Within this containment vessel, ClO concentrations reach 500 times those found at comparable altitudes at midlatitude. Altitude profile at the southern end of the flight trajectories show that the ClO mixing ratio is very steep.
3. Ozone emerges from the austral polar night largely unperturbed. However, within the chemical containment vessel during the first three weeks of September, ozone drops by a factor of two to three such that a strong anticorrelation develops between ClO and O_3 through the wall of the containment vessel.
4. The observed rate of ozone disappearance equals, within experimental uncertainty, the rate limiting step of the ClO-ClO dimer catalytic cycle based on observed concentrations of ClO.